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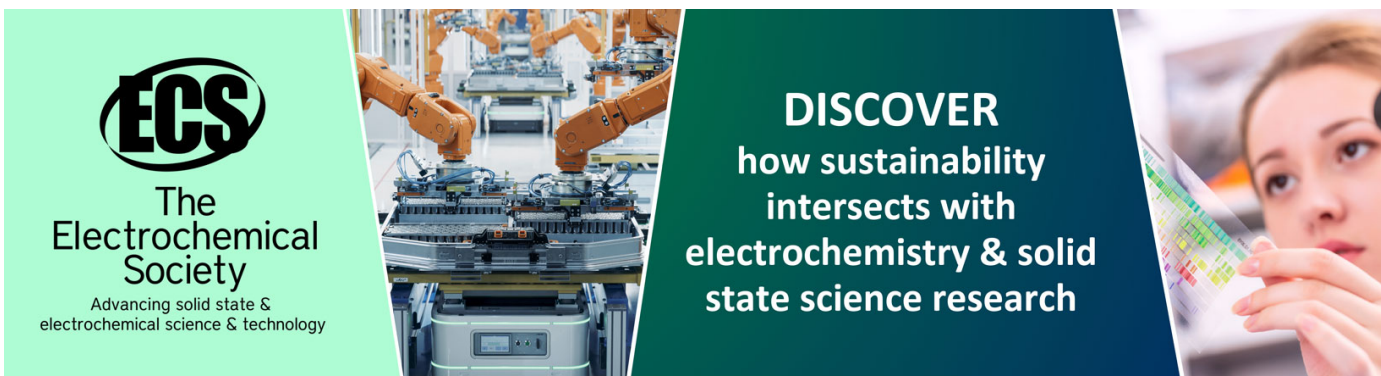
Influence Of The 4d And 5d Transition Metals On The Urbach's Parameters Of Doped $\text{Bi}_{12}\text{SiO}_{20}$

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Influence Of The 4d And 5d Transition Metals On The Urbach's Parameters Of Doped $\text{Bi}_{12}\text{SiO}_{20}$

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Abstract. In this work, the Urbach's rule region (1.77-2.88 eV) in the absorption spectra of doped $\text{Bi}_{12}\text{SiO}_{20}$ is established. The constant of the electron-phonon interaction and the value of the dynamic disorder in the crystal lattice are calculated in the cases of doping with Os, Re, Rh, and Ru. Urbach's energy and the cross-section of the impurity absorption are presented as function of the energy of photons $h\nu$.

1. Introduction

The basic application of the photorefractive $\text{Bi}_{12}\text{SiO}_{20}$ (BSO) single crystals is as holographic information storage [1] and these materials have found application in the field of nonlinear optics [2].

The interest many researchers took in the use of sillenites gave rise to the development of large and optically homogeneous crystal growth techniques. The main objective of optical experiments is to study the influence of different dopant elements on the absorption coefficient and to optimize the physical properties on the basis of practical application. The analysis of the impurity absorption in the

Urbach's rule region is very important because it can answer why some impurities improve the properties of the material they are inculcated in. This work establishes the influence of the impurities Os^{4+} , Re^{4+} , Rh^{4+} , and Ru^{4+} in the region of the Urbach's rule when the crystals are untreated and illuminated with UV light. Their influence is compared with the characteristic Urbach's rule parameters of untreated undoped $\text{Bi}_{12}\text{SiO}_{20}$.

2. Experimental Details

The crystals were prepared from a stoichiometric solution using the Czochralski method. The purity of the starting oxides used was 99.9999% for Bi_2O_3 and SiO_2 . The dopants were placed in the melt solution in the form of oxides: RuO_2 , RhO_2 , PdO , Re_2O_7 and OsO_4 . The concentration of the impurity ions in the crystal lattice was as follows: Os – $1.76 \times 10^{20} \text{ cm}^{-3}$, Re – $1.8 \times 10^{20} \text{ cm}^{-3}$, Rh – $1.63 \times 10^{20} \text{ cm}^{-3}$ and Ru – $3.23 \times 10^{20} \text{ cm}^{-3}$. The diameter of the synthesized crystals was 30-45 mm and their length was 70-100 mm. The experimental set up for the measurement of the absorption coefficient in the visible region consisted of the following: a halogen lamp with a stabilized 3H-7 rectifier, a SPM-2 monochromator, a system of quartz lenses, a polarizer, a crystal sample holder, and a Hamamatsu S2281-01 detector.

3. Results and Discussion

The behaviour of the absorption coefficient α has been investigated at the absorption edge using the Urbach's formula $\ln\alpha = A+B(\hbar\omega/T)$, where A and B are the constants, T is the temperature. The constant B is expressed by the dependence $B = \sigma(T)/k$, where $\sigma(T)$ is the parameter characterizing the slope of the absorption edge, k is the Boltzmann constant. The Urbach's rule or the experimental dependence $\ln\alpha(E)$ for the untreated and illuminated crystals is presented in the spectral region 1.77 – 2.88 eV (figure 1). The Urbach's energy for the undoped and doped sillenites is shown in Figure 2.

The value of $\sigma(T)$ is 0.05 for the untreated crystal, whereas $\sigma(T)$ is higher for the doped with Os, Re and Rh untreated samples (table 1). The parameter $\sigma(T)$ is the lowest for BSO:Ru – 0.04. When the doped samples are illuminated, $\sigma(T)$ for BSO:Re is equal to $\sigma(T)$ for BSO. This parameter decreases for BSO:Re, BSO:Ru and it increases for BSO:Os (table 2).

On the other hand, there is the equation $W_d = kT/\sigma$ [3]. The magnitude W_d describes the broadening of the absorption edge due to the dynamic disorder. When the temperature is higher, the absorption edge is wider due to the dynamic disorder in the crystal lattice. This disorder decreases in the untreated BSO:Os, BSO:Re and BSO:Rh (table 1). It is shown that W_d decreases for the illuminated crystals doped with Os, Re and it increases respectively for BSO:Rh and BSO:Ru (table 2). The parameter $\sigma(T)$ and W_d are calculated at room temperature ($T = 300$ K).

The approximation of the experimental data shows that $\sigma(T) = \sigma_0(2kT/h\nu_0)\text{th}(h\nu_0/2kT)$, where $h\nu_0$ is the energy of the effective phonons, strongly interacting with photons, and σ_0 is the high temperature constant [4]. The magnitude $h\nu_0$ for the crystals under investigation corresponds to the energy $h\nu_0 = 31.7$ meV of the longitudinal optical phonons ($\omega = 257$ cm⁻¹) which are observed in the IR absorption spectra of BSO [5].

In the case under investigation the observed values of σ_0 are as follows: $\sigma_0 = 0.08$ (Bi₁₂SiO₂₀), $\sigma_0 = 0.07 - 0.12$ (the untreated doped Bi₁₂SiO₂₀) (table 1) and $\sigma_0 = 0.05 - 0.12$ (the illuminated doped crystals). The comparison of the values of σ_0 for the samples under investigation with the values of the same constant in [6] shows that the undoped sillenite under investigation has surplus of Bi³⁺ and Bi⁵⁺ ions in the tetrahedral complexes in the crystal lattice. When this crystal is doped with 4d elements the surplus of Bi ions decreases there.

The dependence $g = 2/3\sigma_0$ determines the strength of the electron-phonon interaction [4]. When $g > 1$, the electron-phonon interaction is strong. The value of this strength for the undoped crystal is $g = 8.32$ (Table1). The electron-phonon interaction increases when the untreated crystal is doped with Ru and it decreases for BSO:Os, BSO:Re and BSO:Rh (table 1). When the doped samples are illuminated with UV light, the electron-phonon interaction decreases for BSO:Os and BSO:Re (table 2). The constant g increases for BSO:Rh and BSO:Ru (table 2).

The Urbach's rule region is shifted to the longest wavelengths for all doped samples in the untreated and illuminated state in comparison with the same region of Bi₁₂SiO₂₀ (figure 1).

Urbach's energy is connected with the carrier impurity interaction, the carrier-phonon interaction and the structural disorder [7]. That is why this energy is calculated by the formula $E_u = \alpha(E)/(d\alpha/dE)$. The investigation of the selected crystals leads to the conclusion that Urbach's energy is lower for all untreated and illuminated doped crystals than for the undoped sillenite in the spectral region 1.77-2.88 eV (Figure 2).

The next step in the calculations is the determination of the cross-section of the impurity absorption [8]. It is very important to establish how the radiation is absorbed by the impurity ions in the crystals. The total cross-section σ_a of the impurity absorption is defined by the integration within the absorption band of the impurity ions

$$\sigma_a = \frac{1}{N} \int_{E_1}^{E_2} \alpha(E) dE,$$

where N is the number of the impurity ions in the unit

volume, α is the impurity absorption coefficient typical of an energetic interval from E_1 to E_2 . For the investigated crystals here $E_1 = 1.77$ eV and $E_2 = 2.88$ eV. The cross-section σ_a can vary significantly from one absorption band to another. In the case under investigation the value of the cross section σ_a is the highest for the untreated BSO:Os and the lowest for the untreated BSO:Rh (table 1). The

illumination with UV light proves that σ_a for the doped samples changes as follows: it decreases for BSO:Os, BSO:Ru and it increases for BSO:Re, BSO:Rh (table 2).

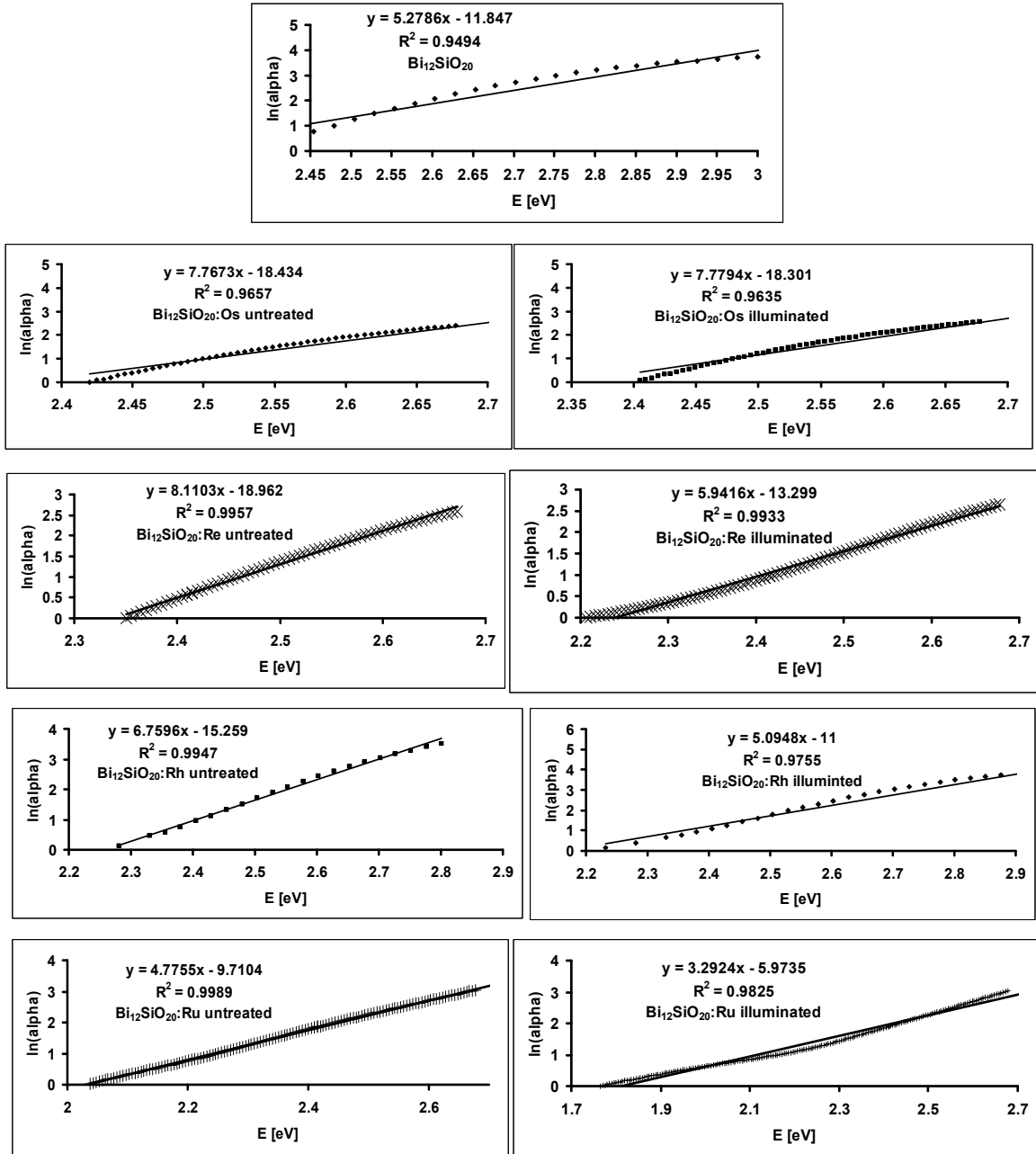
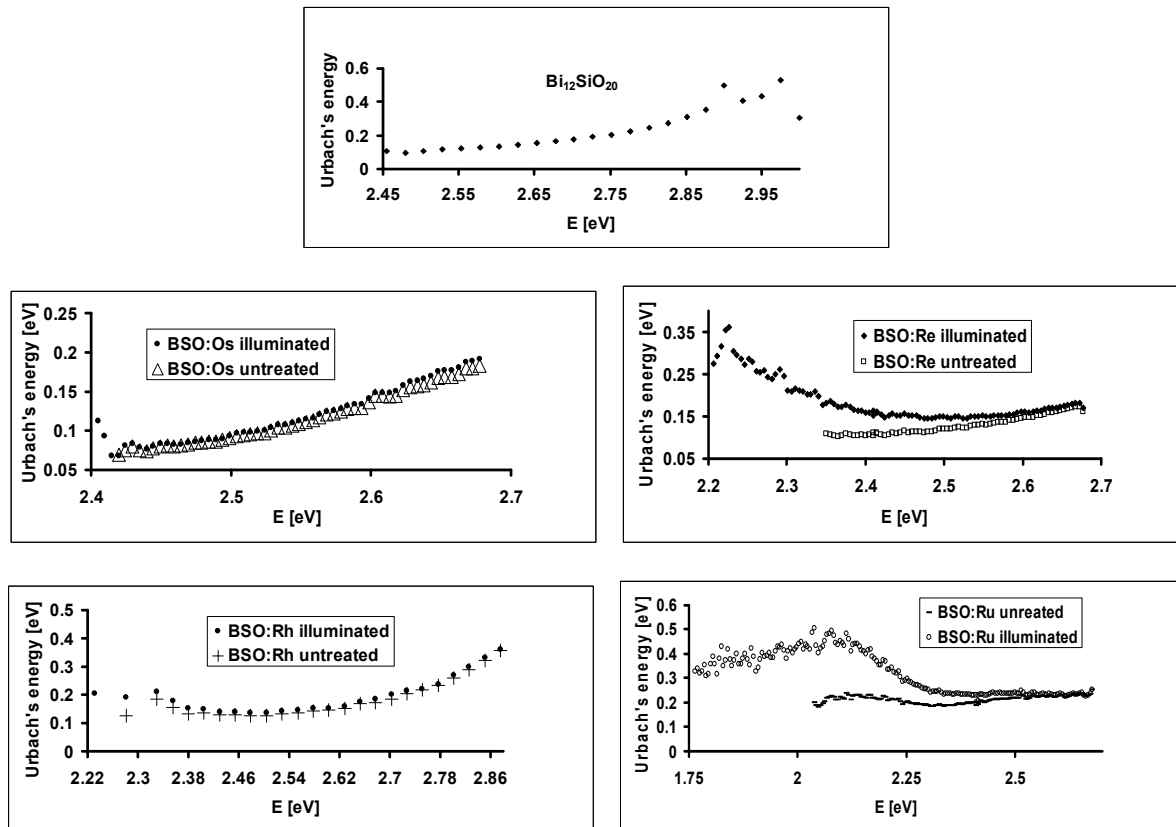


Figure 1. The Urbach's rule region of the untreated and illuminated doped sillenites compared with the same region of untreated undoped BSO.

Table 1. Urbach's parameters of the untreated undoped and doped sillenites.

Untreated Crystals	$\sigma(T)$	σ_0	g	W_d [meV]	σ_a [cm ²]
Bi ₁₂ SiO ₂₀	0.0455	0.0801	8.3229	56 818	-
Bi ₁₂ SiO ₂₀ :Os	0.067	0.118	5.6497	38 585	1.2015x10 ⁻²⁰
Bi ₁₂ SiO ₂₀ :Re	0.0699	0.1231	5.4157	36 984	8.4597x10 ⁻²⁰
Bi ₁₂ SiO ₂₀ :Rh	0.0583	0.1027	6.4914	44 343	13.4601x10 ⁻²⁰
Bi ₁₂ SiO ₂₀ :Ru	0.0412	0.0726	9.1827	62 748	1.3479x10 ⁻²⁰

**Figure 2.** Urbach's energy of the untreated and illuminated doped sillenites compared with the same energy of untreated undoped BSO.**Table 2.** Urbach's parameters of the illuminated doped sillenites.

illuminated doped crystals	$\sigma(T)$	σ_0	g	W_d [meV]	σ_a [cm ²]
Bi ₁₂ SiO ₂₀ :Os	0.067	0.118	5.6497	38 585	1.4136x10 ⁻²⁰
Bi ₁₂ SiO ₂₀ :Re	0.0512	0.0902	7.391	50 492	8.0206x10 ⁻²⁰
Bi ₁₂ SiO ₂₀ :Rh	0.0439	0.0773	8.6244	58 888	13.3483x10 ⁻²⁰
Bi ₁₂ SiO ₂₀ :Ru	0.0284	0.05	13.3333	91 028	1.5657x10 ⁻²⁰

Conclusions

The value of the parameter $\sigma(T)$ is the highest for BSO:Re in an untreated state and for BSO:Os in the illuminated state. Thus the conclusion is that the number of the longitudinal phonons is the biggest for the same doped crystals. The value of the electron-phonon interaction constant is the highest for the Ru doped sample in the untreated and illuminated state. The dynamic disorder in the crystal lattice is again the biggest in BSO:Ru in the untreated and illuminated state. Urbach's energy of the untreated crystal does not change its curvature for BSO:Os and BSO:Re in the untreated and illuminated state.

The same energy changes the slope of its curvature for BSO:Re and BSO:Ru in the illuminated state. The cross-section of the impurity absorption σ_a is the highest for BSO:Os and its value is the lowest for BSO:Rh in the untreated and illuminated state.

Acknowledgement

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